Failure of intramolecular energy relaxation in unimolecular reaction systems*

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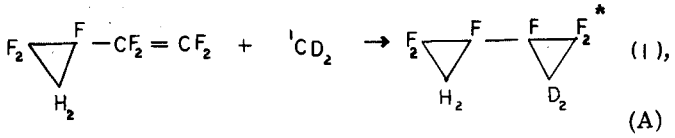
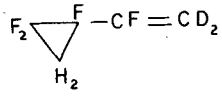
We describe here a novel and comprehensive demonstration of the failure of internal randomization of energy in a series of decomposing fluoroalkyl cyclopropanes.

Recently, Rynbrandt and Rabinovitch[1] reported the demonstration of failure of neutral molecules to complete intramolecular energy randomization prior to decomposition. In that work, chemically activated fluorinated bicyclopropane molecules having isotopically labeled rings were formed by reaction with methylene radicals,



(I), (A)

and also by the isotopically interchanged counterpart reaction with $^1CH_2$ which put the 2 H atoms into the nascent ring. The hot molecule can decompose by CF_2 split off from either ring. Upon activation, energy deposition occurred in the D-labeled nascent ring of I which underwent preferential (nonrandomized) decomposition to the extent of ~3.5% of the total activated substrate to form excess of



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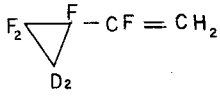
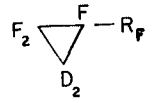


the inverse proportion arose from the isotopic counterpart system. Thus, decomposition of the unrelaxed nascent ring competed with intramolecular relaxation at short elapsed times. From their data, the relaxation time for internal energy randomization was calculated by RR as $\tau \sim 9\times10^{-13}$ sec.

It is not the case that an experimental test of nonrandomization will automatically reveal[2] such failure if carried out at very short times (high pressures). Indeed, most nonbeam studies have failed to confirm such an effect[3,4] or are of uncertain result.[5,6] The present study provides both an important confirmation of the earlier result of RR, together with a more comprehensive demonstration of the failure of randomization, and extension to higher pressures where collisional interception of the nonrandomized species can occur.

A series of fluoroalkyl cyclopropanes



were prepared as in Reaction (A) by addition of $^1CD_2$ (produced by the photolysis at 2900 Å of ketene-d_2 at 25 °C) to $R_FCF=CF_2$, where $R_F \equiv CF_3$, C_3F_7, and C_5F_{11}. CO was used as inert bath gas. Triplet methylene was scavenged by addition of a small amount of oxygen. The simplest hypothesis from the work of RR is that the nascent ring moiety will in every case decompose at an initial rate found by them to be $\sim 3\times10^{11}$ sec^{-11}; the theoretical rates (see below) of decomposition of the randomized molecules are, respectively, 6.74×10^9, 3.11×10^7, and 3.76×10^5 sec^{-1}. Define[7] an apparent decomposition rate constant as $k_a = \omega D/S$, where ω is the rate of deactivating collisions (corrected for weak collider inefficiency[1]) and D and S are olefin decomposition product and collisionally stabilized alkyl cyclopropane, respectively. Then, since $D = D_{NR} + D_R$, where D_{NR} is a constant "nonrandomized" component of decomposition of the moiety and D_R is the amount of normal, collisionally interceptible[7] decomposition of the relaxed molecule, it is predicted that k_a should increase with increase of pressure in a given system due to the constant component D_{NR}. The experiment provides a measure of D_{NR} and of τ. In the case that $D_{NR} \ll D_R$, then $k_a \simeq k_R$; this is the situation at low pressures.

In Fig. 1 is shown the variation of k_a with ω. The experimental data are in reasonable agreement with a theoretical model in which a constant value of $\tau = 9\times10^{-13}$

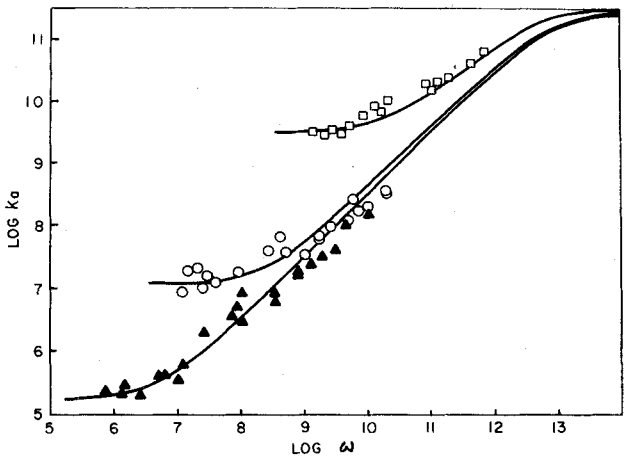


FIG. 1. Plot of k_a (log scale) vs ω for $R \equiv CF_3$, □, C_3F_7, ○, and C_5F_{11}, ▲, showing different regions of increase of k_a. The solid curves are theoretical computations with a single relaxation time, $\tau = 8.8\times10^{-13}$ sec.

sec^{-1}, the same value as given by RR, is employed for all systems. The calculative method followed that of RR with minor improvements. Satisfactory agreement, within a factor of 2.5 (all on the high side), is found between RRKM theoretical values of k_R for each system, based upon a transition state model similar to that of RR, and the experimental values which range over a factor of 2×10^4 from $R_F \equiv CF_3$ (2.9×10^9 sec^{-1}) to $R_F \equiv C_5F_{11}$ (1.7×10^5 sec^{-1}). The experimental values of k_R were adopted for the detailed comparison of experiment with theory for the increase in k_a at higher pressures. The amount D_{NR} is measured as 12.5% for CF_3, 3% for n-C_3F_7, and 2% for n-C_5F_{11}; the theoretical quantities are 9.8%, 4.2%, and 3.2%, respectively. In view of the experimental scatter and of the uncertainty in energetics and other features of the simplified model we have used, the agreement in Fig. 1 is even better than should be expected. Less than strong collisions by CO cause a slight, but negligible, decrease in the estimated relaxation time.

It is important to note that whereas the work of RR did not extend to sufficiently high pressure so that collisional stabilization of the nascent nonrandomized species did not occur, the present work for $R_F \equiv CF_3$ was carried to 72 atm pressure and collisional stabilization of the nonrandomized entity became significant. Full details and discussion of the calculations and some alternative choices for parameters will be described later.

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